ELEMENTAL ANALYSIS OF COMBUSTION PRODUCTS BY NEUTRON ACTIVATION

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Environmental Sciences Division of Lawrence Livermore Laboratory is
engaged in a study of the environmental impact of effluent by-products
resulting from various methods of energy production. Included in the
overall study are three methods- coal-fired power plants operation, oil
shale retort operations, and underground coal gasification- which produce
combustion products. One of our primary interests is the elemental
composition of these products and we use several analytical techniques
to obtain as complete an elemental profile as possible. Atomic absorption,
X-ray Fluorescence, Induction Coupled Plasma-Optical Emission Spectroscopy,
and Ion Chromatography are all routinely employed in the analytical
program. However the main analytical method has been absolute Instrumental
Neutron Activation Analysis (INAA) with the other techniques being used
to fill out missing elements in the overall scheme. A brief description
of the neutron activation analysis method is given below.

Basically, absolute INAA is dependent upon the absolute measurement
of the disintegration rates of the nuclides produced by neutron capture.
From such disintegration rate data, the amount of the target element
present in the irradiated sample is calculated by dividing the observed
disintegration rate for each nuclide by the expected value for the
disintegration rate per microgram of the target element that produced
the nuclide.

In absolute INAA, the expected value for disintegration rate per
microgram is calculated from nuclear parameters and from measured values
of both thermal and epithermal neutron fluxes which were present during
irradiation. Absolute INAA does not depend on the concurrent irradiation

of elemental standards but does depend on the values for thermal and epithermal neutron capture cross-sections for the target nuclides.

Using the element cobalt and its neutron capture product ^{60}Co as examples, the basic equation for absolute INAA can be expressed as follows:

$$\text{Micrograms Cobalt} = \frac{\text{Measured DPM } ^{60}\text{Co}}{\text{Expected DPM } ^{60}\text{Co/}\mu\text{g Cobalt}} \qquad (1)$$

The numerator on the right side of the equation is determined by analyzing the gamma spectrum of an irradiated sample to find absolute disintegration rates for each of the contributing nuclides. At LLL this analysis is carried out by a computer program GAMANAL which was developed by R. Gunnink and J. Niday. GAMANAL is described in detail in UCRL-51061(1).

All of the gamma spectrometer systems used in this program use lithium-drifted Germanium detectors, and are calibrated to measure absolute photons per minute as a function of photon energy and source geometry. The spectrum, which covers the energy range 50 Kev to 2000 Kev, consists of 4096 channels at 0.5 Kev per channel. In the spectral analysis, GAMANAL determines the energies and absolute intensities of the gamma rays by determining a background and fitting peaks using a prescribed peak shape function. Complex groups are resolved by a least squares fitting method. At this point the spectrum has been reduced to a set of gamma ray energies and total intensities. The next step is to interpret these energies and intensities in terms of disintegration rates of specific nuclides.

Interpretation by GAMANAL is a two step process. First, a tentative identification of the radionuclides present is made by comparing the observed energies with energies listed in a decay scheme library. The library contains half-life and parent-daughter relationships for each nuclide and branching intensity of its gamma rays. GAMANAL uses energy, half-life vs sample age and associative gammas to generate a list of candidate nuclides which could have produced the set of observed gamma rays. In the final step, a matrix of equations is set up on the basis that each observed photopeak is a linear combination of one or more components arising from the list of nuclides tentatively identified. A least-squares solution of the set of equations produces the final result of the gamma spectrum analysis - a list of disintegration rates of specific nuclides.

The denominator term on the right side of equation (1) is determined by calculating the radionuclide production rate by both thermal and epithermal neutrons, and correcting for radioactive growth and decay processes as required by the irradiation, cooling, and counting times. The computations are carried out by means of a computer program, NADAC, developed by R. Heft and W. Martin and is described in detail in UCRL-52249(2).

The overall analysis is carried out in the following manner. The sample to be analyzed is irradiated for a measured interval of time. The irradiation package includes a dual flux monitor consisting of two nuclides. For one nuclide the ratio of the epithermal neutron capture cross-section to the thermal neutron capture cross-section must be small (e.g. ^{46}Sc with a ratio equal to 0.44). For the other nuclide the ratio must be high (e.g. ^{238}U with a ratio equal to 102.9). Following a

cooling period, the gamma spectral analysis is started and continued for a measured real time interval. The gamma spectrum is analyzed by GAMANAL and the output listing of disintegration rates at counting time for the nuclides found is used as input to NADAC. A separate spectral analysis of the dual flux monitor is made in order to determine both thermal and epithermal neutron flux values. These and the required irradiation, cooling, and counting time values are also provided to NADAC which combines the experimental data with stored values of the nuclear parameters and computes total micrograms for each element, corrected as required for interference by (n,p) or (n,f) reactions. NADAC uses an absolute computation method and provides a correct calculation of elemental abundance in all cases including:

- Counting time is long compared to half-life of radionuclide counted.

- Sample is subjected to multiple or interrupted irradiations.

- Nuclide counted is daughter of nuclide produced, including the case where daughter is also produced directly.

A variety of sample types are generated by the expermental programs. The samples are prepared for irradiation with a minimum of handling and are separated from whatever container was used during the irradiation before being gamma counted. Samples fall into three main categories:

Bulk Solid Samples.

Coal, flyash, shales etc. are dried, ground in agate mortar, and pelletized using microcrystalline cellulose as Binder, ∿100mg -1gm samples.

Bulk liquid samples.

Oils and high level waters are sealed into 5-15ml polyethylene vials for irradiation and transferred prior to counting. Low level waters are

are evaporated onto microcrystalline cellulose and pelletized. Internal tracer is used.

Limited samples.

Impactor stages, air filters, charcoal trap sections etc. are irradiated as collected with substrate. Substrate blank must be determined and corrected for.

Samples are subjected to whatever irradiation, cooling, and counting schedules are appropriate for the elements sought. For maximum number of elements two irradiation and ensuing counting periods are used. The first is a short irradiation (less than 10 minutes duration) followed by a 10 minute cool and 10, 20, and 40 minute sequential counts. The second is a long irradiation (one to six hours) counted at three and fifteen days for 6000 and 20000 seconds.

The elements found by this method of analysis will vary from sample to sample but in general the set of elements found is exemplified by the following which were obtained from analyses of both raw shale and fly ash.

Standard Deviation	Elements Found (Ordered by atomic number)
Less than 2%	Na, Al, K, Sc, Cr, Mn, Fe, Co, As, Rb, Sb, Cs Ba, La, Ce, Sm, Eu Yb, Hf, Th
2% to 10%	V, Zn, Ga, Se, Br, Sr, Mo, Nd, Tb, Dy, Ta
10% to 40%	Ti, Ni, Zr, Gd, W

The above lists represents elements which can be measured by absolute INAA where sample amount is not a limiting factor and where a broad spectrum of elements is in the sample.

Literature Cited

(1) Gunnink, R., and Niday, J., Computerized Quantitative Analyses by Gamma Ray Spectrometry. UCRL-51061, Lawrence Livermore Laboratory, Livermore, California (1972).

(2) Heft, R., and Martin, W., NADAC and MERGE-Computer Codes for Processing Neutron Activation Analysis Data, UCRL-52249, Lawrence Livermore Laboratory, Livermore, California (1977).